Inorganic Chemistry
Communication

Valence-Tautomeric Ionic Liquid Composed of a Cobalt Bis(dioxolene) Complex Dianion

Yukihiro Yoshida,*[†,‡] Hirofusa Tanaka,[‡] Gunzi Saito,*[†,‡] Lahcène Ouahab,[§] Hiroyuki Yoshida,[⊥] and Naoki Sato[⊥]

[†]*Research Institute, Meijo University, Shiogamaguchi 1-501, Tempaku, Nagoya 468-8502, Japan,*
[‡]*Division of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan,*
[§]*Organométalliques et Matériaux Moléculaires, Matériaux Inorganiques Multifonctionnels, UMR6226 CNRS,*
Université de Rennes 1, 263 Avenue Général Leclerc, CS74205, 35042 Rennes Cedex, France, and
[⊥]*Institute for Chemical Research, Kyoto University, Uji 611-0011, Japan*

We successfully synthesized a room-temperature ionic liquid showing valence-tautomeric behavior, by combining a cobalt bis-(dioxolene) complex dianion with a bulky trihexyl(tetradecyl)phosphonium cation. Its magnetic moment exhibits a gradual increase up to ca. 280 K through the glass transition (262 K) and then has an abrupt upturn at around 300 K. The valence-tautomeric behavior was confirmed by the temperature dependence of the electronic absorption spectra. This successful implementation allowed the "smart" ionic liquid, whose magnetic behavior responds evidently to temperature change.

The molecular design of ionic liquids, which are entirely composed of ions and melt below room temperature (RT) or 100 °C, appears to be one of the main challenges in materials chemistry.[1] A special fascination of the ionic liquids is that the selection of component ions allows us not only to control their physicochemical properties but also to impart new functionalities that have not previously been available in conventional molecular solvents. In this context, we have reported,[2] along with others,[3] ionic liquids with paramagnetic properties, using magnetoactive anions such as $Fe^{III}X_4^-$ (X = Cl, Br),[2a–c] $Co^{II}X_4^{2-}$ (X = Cl, N(CN)$_2$, NCS),[3a,b] $Dy^{III}(SCN)_{8-x}(H_2O)_x^{(5-x)-}$ ($x = 0-2$),[3c] and TEMPO-OSO$_3^-$ (2,2,6,6-tetramethyl-1-piperidinyloxyl-4-sulfate).[2d] For the last case, the introduction of an acidic sulfate group to a neutral TEMPO radical moiety leads to the organic radical anion and, subsequently, the first organic paramagnetic ionic liquids.[2d] In the present study, using this synthetic approach, we proceed our study to the next stage, namely, the development of ionic liquids that can modify the magnetic behavior by applying external stimuli, e.g., temperature, pressure, electric field, and light irradiation. Such a "smart fluid" has become increasingly important as potential systems for micro- and nanofluidic devices,[4] and some "smart" ionic liquids, i.e., those showing changes in the ionicity, polarity, viscosity, and ionic conductivity caused by exposure to CO_2[5] and decreases in miscibility caused by heat (lower critical solution temperature),[6] have been found. However, there has been no ionic liquid whose physical properties vary markedly with temperature.

Octahedral cobalt bis(dioxolene) valence tautomers, Co^{III}-(DBCat)(DBSQ)(N–N), where $DBCat^{2-}$ and $DBSQ^{•-}$ refer to dianionic 3,5-di-*tert*-butyl-1,2-catecholate and monoanionic 3,5-di-*tert*-butyl-1,2-semiquinonate, respectively, and N–N is a nitrogen–nitrogen bidentate ligand, interconvert

*To whom correspondence should be addressed. E-mail: yyoshida@ccmfs.meiho-u.ac.jp.

(1) (a) *Ionic Liquids in Synthesis*; Wassersscheid, P., Welton, T., Eds.; Wiley-VCH: Weinheim, Germany, 2003. (b) *Electrochemical Aspects of Ionic Liquids*; Ohno, H., Ed.; John Wiley and Sons: Upper Saddle River, NJ, 2005. (c) Wasserscheid, P.; Keim, W. *Angew Chem., Int. Ed.* **2000**, *39*, 3772–3789. (d) Buzzeo, M. C.; Evans, R. G.; Compton, R. G. *ChemPhysChem* **2004**, *5*, 1106–1120. (e) Davis, J. H. *Chem. Lett.* **2004**, *33*, 1072–1077. (f) Fei, Z.; Geldbach, T. J.; Zhao, D.; Dyson, P. J. *Chem. Eur. J.* **2006**, *12*, 2122–2130.

(2) (a) Yoshida, Y.; Fujii, J.; Muroi, K.; Otsuka, A.; Saito, G.; Takahashi, M.; Yoko, T. *Synth. Met.* **2005**, *153*, 421–424. (b) Yoshida, Y.; Otsuka, A.; Saito, G.; Natsume, S.; Nishibori, E.; Takata, M.; Sakata, M.; Takahashi, M.; Yoko, T. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 1921–1928. (c) Yoshida, Y.; Saito, G. *J. Mater. Chem.* **2006**, *16*, 1254–1262. (d) Yoshida, Y.; Tanaka, H.; Saito, G. *Chem. Lett.* **2007**, *36*, 1096–1097.

(3) (a) Del Sesto, R. E.; Corley, C.; Robertson, A.; Wilkes, J. S. *J. Organomet. Chem.* **2005**, *690*, 2536–2542. (b) Del Sesto, R. E.; McCleskey, T. M.; Burrell, A. K.; Baker, G. A.; Thompson, J. D.; Scott, B. L.; Wilkes, J. S.; Williams, P. *Chem. Commun.* **2008**, 447–449. (c) Mallick, B.; Balke, B.; Felser, C.; Mudring, A.-V. *Angew. Chem., Int. Ed.* **2008**, *47*, 7635–7638.

(4) (a) Atencia, J.; Beebe, D. J. *Nature* **2005**, *437*, 648–655. (b) Abgrall, P.; Nguyen, N. T. *Anal. Chem.* **2008**, *80*, 2326–2341.

(5) (a) Jessop, P. G.; Heldebrant, D. J.; Li, X.; Eckert, C. A.; Liotta, C. L. *Nature* **2005**, *436*, 1102. (b) Yamada, T.; Lukac, P. J.; George, M.; Weiss, R. G. *Chem. Mater.* **2007**, *19*, 967–969. (c) Phan, L.; Chiu, D.; Heldebrant, D. J.; Huttenhower, H.; John, E.; Li, X.; Pollet, P.; Wang, R.; Eckert, C. A.; Liotta, C. L.; Jessop, P. G. *Ind. Eng. Chem. Res.* **2008**, *47*, 539–545.

(6) (a) Lachwa, J.; Szydlowski, J.; Najdanovic-Visak, V.; Rebelo, L. P. N.; Seddon, K. R.; Nunes de Ponte, M.; Esperança, J. M. S. S.; Guedes, H. J. R. *J. Am. Chem. Soc.* **2005**, *127*, 6542–6543. (b) Fukumoto, K.; Ohno, H. *Angew. Chem., Int. Ed.* **2007**, *46*, 1852–1855.

(7) (a) Pierpont, C. G.; Buchanan, R. M. *Coord. Chem. Rev.* **1981**, *38*, 45–87. (b) Pierpont, C. G. *Coord. Chem. Rev.* **2001**, *216–217*, 99–125. (c) Dei, A.; Gatteschi, D.; Sangregorio, C.; Sorace, L. *Acc. Chem. Res.* **2004**, *37*, 827–835. (d) Evangelio, E.; Ruiz-Molina, D. *Eur. J. Inorg. Chem.* **2005**, 2957–2971. (e) Sato, O.; Tao, J.; Zhang, Y.-Z. *Angew. Chem., Int. Ed.* **2007**, *46*, 2152–2187.

Scheme 1. Valence-Tautomeric Bistability of the Present Cobalt Complex Dianion
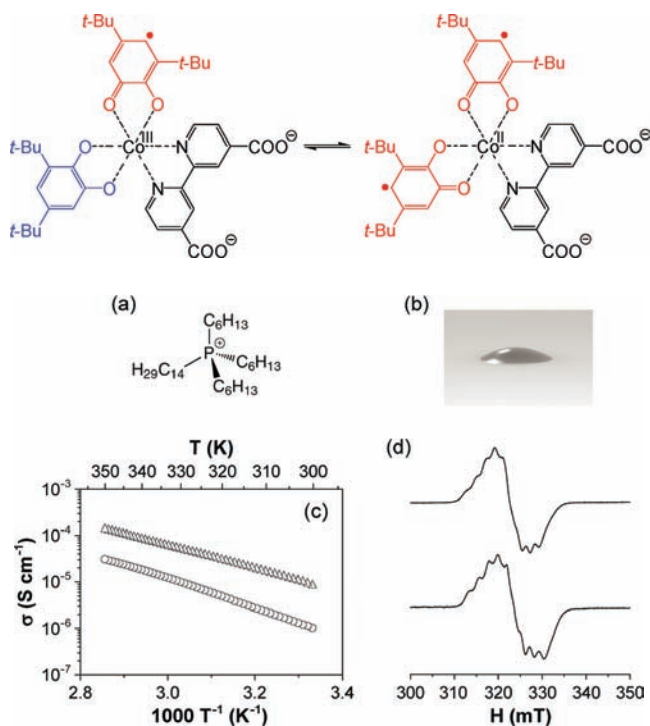
Figure 1. (a) Molecular structure of a $P_{14,6,6,6}$ cation. (b) Photograph on a polypropylene sheet. (c) Temperature dependence of the ionic conductivity (σ) on the heating process. The conductivity data (circles) were compared with those of $[P_{14,6,6,6}]$Cl (triangles). (d) ESR spectra measured at 100 K for $[P_{14,6,6,6}]_2[Co(DBCat)(DBSQ)(DCOObpy)]$ (upper, neat glass; lower, 10^{-3} M toluene glass).

between a low-spin Co^{III} ($S = 0$) system with one unpaired electron on a DBSQ ligand and a high-spin Co^{II} ($S = {}^3/_2$) system with two unpaired electrons on DBSQ ligands.[7] Such a phase equilibrium has potential applicability for molecular devices such as information storage and switches and could be driven by either temperature change or light irradiation.[7] We here combined the cobalt bis(dioxolene) unit with 2,2′-bipyridine (bpy) having two carboxylate groups at the 4 positions as N−N to realize an ionic liquid showing valence-tautomeric behavior (Scheme 1).

Highly viscous (>1000 mPa s), dark-green liquid $[P_{14,6,6,6}]_2[Co(DBCat)(DBSQ)(DCOObpy)]$ (Figure 1b) was synthesized by the reaction of stoichiometric amounts of dark-green crystalline $[Co(DBSQ)_2]_4 \cdot 2PhH^8$ and pale-yellow liquid $[P_{14,6,6,6}]_2[DCOObpy]$ in anhydrous ethanol in an inert atmosphere (see the Supporting Information), where $P_{14,6,6,6}$ and DCOObpy are a trihexyl(tetradecyl)phosphonium cation (Figure 1a) and a 2,2′-bipyridine-4,4′-dicarboxylate dianion, respectively. No traces of Na, Ag, and Cl, which were included in the precursors, were detected for energy-dispersive X-ray spectroscopy.

The differential scanning calorimetry trace of the salt shows a glass transition at $T_g = 262$ K during the heating process, and no crystallization and melting events were detected because of the long alkyl chains in the cation. It decomposes at around 350 K, providing the liquid range of ca. 90 K.

(8) Buchanan, R. M.; Fitzgerald, B. J.; Pierpont, C. G. *Inorg. Chem.* **1979**, *18*, 3439–3444.
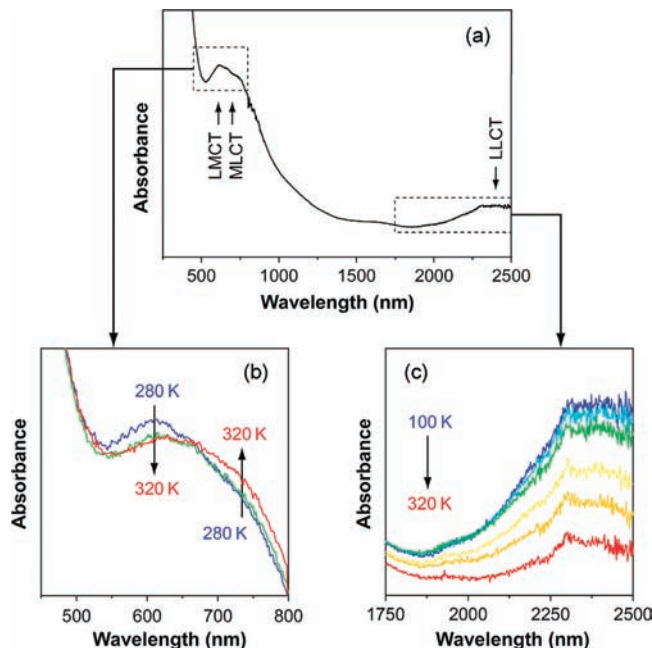
Figure 2. (a) Electronic absorption spectrum of $[P_{14,6,6,6}]_2[Co(DBCat)-(DBSQ)(DCOObpy)]$ at 100 K, measured with a KBr compressed pellet. Temperature dependence of the spectra (b) in the high-energy region (280, 300, and 320 K) and (c) in the low-energy region (100, 200, 260, 280, 300, and 320 K).

The ionic conductivity (σ) at RT (300 K) was determined to be 1.03×10^{-6} S cm^{-1} and is significantly low in comparison with that of $[P_{14,6,6,6}]$Cl (8.94×10^{-6} S cm^{-1}) because of the bulky dianions. As seen in Figure 1c, the temperature dependence follows the Arrhenius equation $\sigma = \sigma_0 \exp(-E_a(\sigma)/k_B T)$, with a constant σ_0 of 10.4 S cm^{-1} and an activation energy for ionic conduction $E_a(\sigma)$ of 0.625 eV, over the measured temperature range (300−350 K).

Figure 1d shows the X-band electron-spin resonance (ESR) spectra measured at 100 K. The neat sample shows a broad isotropic signal ($\Delta H_{pp} \sim 80$ Oe) at $g = 2.000$ with a ^{59}Co ($I = {}^7/_2$) hyperfine structure ($A = 19$ Oe) as seen for the diluted toluene solution (10^{-3} M), and both spectra are closely similar to that of the diluted solution of Co(DBCat)-(DBSQ)(N−N).[9] The presence of bulky phosphonium cations must be a significant part of the reason for the hyperfine structure. The signal gradually decreases as the temperature rises through the glass transition, with the line width remaining unchanged.

Figure 2a shows an electronic absorption spectrum at 100 K, measured with a KBr compressed pellet. The spectrum is also reminiscent of that of Co(DBCat)(DBSQ)-(N−N).[9,10] At low temperatures, a band chracteristic of a ligand-to-metal charge transfer (LMCT) from the catecholate to the central cobalt[9b,10b] was observed at around 610 nm. As the temperature increases from 280 to 320 K, the intensity of the 610 nm band apparently decreases, while a band at around 740 nm increases in intensity (Figure 2b).

(9) (a) Jung, O.-S.; Pierpont, C. G. *Inorg. Chem.* **1994**, *33*, 2227–2235. (b) Adams, D. M.; Noodleman, L.; Hendrickson, D. N. *Inorg. Chem.* **1997**, *36*, 3966–3984. (c) Jung, O.-S.; Jo, D. H.; Lee, Y.-A.; Sohn, Y. S.; Pierpont, C. G. *Inorg. Chem.* **1998**, *37*, 5875–5880.
(10) (a) Adams, D. M.; Dei, A.; Rheingold, A. L.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1993**, *115*, 8221–8229. (b) Adams, D. M.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1996**, *118*, 11515–11528.
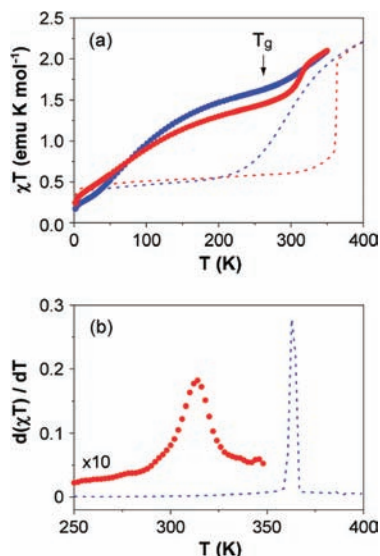
Figure 3. (a) Temperature dependence of χT (χ = static susceptibility) for [$P_{14,6,6,6}$]$_2$[Co(DBCat)(DBSQ)(DCOObpy)] on heating (red circles) and cooling (blue circles) processes under an applied magnetic field of 1 T. A vertical arrow indicates the glass transition temperature (T_g = 262 K). Dotted lines indicate the temperature dependence for polycrystalline Co(DBCat)(DBSQ)(bpy) on heating (red) and cooling (blue) processes. (b) Temperature dependence of $\mathrm{d}(\chi T)/\mathrm{d}T$ for [$P_{14,6,6,6}$]$_2$[Co(DBCat)-(DBSQ)(DCOObpy)] (red circles) and Co(DBCat)(DBSQ)(bpy) (blue dotted line) during the heating process. The former values increase 10-fold to facilitate visualization.

Considering the fact that the 740 nm band is associated with a metal-to-ligand charge transfer (MLCT) from the central cobalt to semiquinonate,[9b,10b] this spectral change indicates that the present salt exhibits a valence-tautomeric equilibrium in the liquid state at around 300 K, which exceeds substantially the glass transition temperature (262 K). The presence of an isosbestic point (ca. 670 nm) would confirm two different species in equilibrium. As expected, a low-energy band (ca. 2400 nm), which is ascribed to mixed-valence intervalence charge transfer from the catecholate to semiquinonate ligands (ligand-to-ligand charge transfer; LLCT),[9b,10b] gradually decreases in intensity with increasing temperature, obviously above 260 K (Figure 2c).

The product of static susceptibility (χ) and temperature as a function of temperature is depicted in Figure 3a. The χT value at 2 K (0.25 emu K mol^{-1}) falls into the range of values expected for the $S = {}^1/_2$ unpaired spin (the spin-only value is 0.375 emu K mol^{-1}). With increasing temperature, it exhibits a gradual increase of up to ca. 280 K through the glass transition (262 K). Above 280 K, there is an abrupt upturn of χT, which then begins to approach the value expected for an uncorrelated three-spin system with $S = {}^1/_2, {}^1/_2$, and ${}^3/_2$ (the spin-only value is 2.625 emu K mol^{-1}), without magnetic saturation. Such a temperature dependency is rather different from that of polycrystalline valence-tautomeric complex Co(DBCat)(DBSQ)(bpy) (dotted lines in Figure 3a) but reminds us of that of the colloidal suspension of nanoparticles

composed of valence-tautomeric coordination polymer Co-(DBCat)(DBSQ)(bix), where bix is 1,4-bis(imidazol-1-yl-methyl)benzene.[11] It should be noted that the observed valence tautomerism has little impact on the ion diffusivity because no anomaly was observed for σ in this temperature region.

There might be two qualitative explanations regarding the lower equilibrium temperature, namely, the higher stability of the high-spin Co^{II} state, for [$P_{14,6,6,6}$]$_2$[Co-(DBCat)(DBSQ)(DCOObpy)] compared to Co(DBCat)-(DBSQ)(bpy) (Figure 3b). One is the introduction of electron-withdrawing carboxylate groups to bpy, which leads to the reduced coordination ability of bpy and, subsequently, the reduced ligand field around Co ions. The other is associated with the loose molecular packing in the liquid state, which also allows for stabilization of the high-spin Co^{II} complex dianions with a larger volume than low-spin Co^{III} complex dianions.[10a] This effect is supported by the increase in the equilibrium temperature for some Co(DBCat)-(DBSQ)(N−N) with increasing applied hydrostatic pressure.[12] It is also noteworthy that cobalt bis(dioxolene) complexes composed of pyridines with long alkoxy groups exhibit the valence-tautomeric behavior coupled with the melting event.[13]

On cooling from 350 K, the χT value gradually decreases to 2 K, without any anomaly at around 280−320 K. Such thermal hysteresis was absent when cooled from 300 K. Whereas the correlation between the valence-tautomeric behavior and the glass transition remains unclear at the present stage, the observed thermal hysteresis gives us firm evidence of RT magnetic bistability in the liquid state. The high-χT state was kept for less than 1 day at RT.

In summary, we synthesized a RT ionic liquid showing valence-tautomeric behavior, by combining a cobalt bis(dioxolene) complex dianion with a bulky tetraalkyl-phosphonium cation. The successful implementation allowed the smart ionic liquid, whose magnetic susceptibility responds evidently to temperature change.

Supporting Information Available: Experimental details and syntheses and characterizations of [$P_{14,6,6,6}$]$_2$[DCOObpy] and [$P_{14,6,6,6}$]$_2$[Co(DBCat)(DBSQ)(DCOObpy)]. This material is available free of charge via the Internet at http://pubs.acs.org.

(11) Imaz, I.; Maspoch, D.; Rodríguez-Blanco, C.; Pérez-Falcón, J. M.; Campo, J.; Ruiz-Molina, D. *Angew. Chem., Int. Ed.* **2008**, *47*, 1857–1860.

(12) (a) Roux, C.; Adams, D. M.; Itié, J. P.; Polian, A.; Hendrickson, D. N.; Verdaguer, M. *Inorg. Chem.* **1996**, *35*, 2846–2852. (b) Caneschi, A.; Dei, A.; Fabrizi de Biani, F.; Gütlich, P.; Ksenofontov, V.; Levchenko, G.; Hoefer, A.; Renz, F. *Chem.—Eur. J.* **2001**, *7*, 3926–3930. (c) Gütlich, P.; Gaspar, A. B.; Ksenofontov, V.; Garcia, Y. *J. Phys.: Condens. Matter.* **2004**, *16*, S1087–S1108.

(13) Kiriya, D.; Chang, H.-C.; Kitagawa, S. *J. Am. Chem. Soc.* **2008**, *130*, 5515–5522.